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Porous Alumina Template based Versatile and Controllable Direct Synthesis of Silicon nanowires

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ABSTRACT

Highly densely packed, self-organized silicon nanowires with very narrow diameter distribution were synthesized within porous anodic alumina templates with electrodeposited catalytic metal nanoparticles. For successful catalytic metal nanoparticle deposition, electrochemical-, and chemical barrier layer thinning process was investigated following anodization process. Controlled pulsed electrodeposition process was carried out for a volume calibration of desired catalytic metal nanoparticle deposition inside nanopore arrays using different metal-ion containing electrolyte. Not only single metal nanoparticles, but also multi metal nanoparticles layers were filled inside PAA to enhance metal filling aspect, and to control the volume of nanoparticles more precisely. Using multilayered metal nanoparticles resulted on different SiNW's growth behavior depending on the types of underlying metal nanoparticles.

SiNWs were successfully synthesized using hot-filament assisted chemical vapor deposition system. Although silicon precursor gas can generally be dissociated at relatively low temperatures, the use of a hot filament activation help decreasing process temperature, and also, highly activated atomic hydrogen generation via the tungsten hot filament placed at gas inlet helps preventing parasitic amorphous silicon deposition on either the alumina membrane surface or the pore wall which hinders appropriate growth of SiNWs in PAA by nanopores clogging. Such densely packed, self-organized SiNWs are of high interest in many application fields like nanoelectronics, optoelectronics, and energy storage/conversion devices etc.

INTRODUCTION

Quasi one-dimensional (1-D) semiconducting nanowires such as silicon(Si), germanium(Ge), gallium arsenide(GaAs), indium phosphide (InP), cadmium selenide(CdSe) nanowires are of high interest as alternative materials for future electronics[1]. Especially silicon nanowires(SiNWs) have been considered one of the most promising materials as building blocks for future nanoelectronics, optoelectronics, and energy storage/conversion devices due to their excellent physical, electrical, and optical properties. SiNWs have already demonstrated high potential for application in field-effect transistors(FETs) [2], solar cells[3], chemical and biosensors[4], Li-ion battery electrode[5] and so on. Nowadays SiNW-based devices are fabricated following both top-down[6] and bottom-up[6] approaches. The top-down approach combines high quality of SiNWs and uniform array fabrication, but the process is time consuming, and poor substrate flexibility is available. On the contrary, the bottom-up approach, especially chemical vapor deposition(CVD) based process, has recently shown high potential to synthesize semiconductor nanowires for future applications[6]. For such CVD process, metal

catalyzed synthesis process via vapor-liquid-solid(VLS) process is a popular method in order to control the density, aspect ratio, and alignment of SiNWs[7]. High density and uniformly organized SiNWs synthesis is a key issue for many applications. Various methods to control the density and the size of SiNWs have been reported. Among them, the template-based approach using porous anodic alumina (PAA) template has been recently[8] investigated due to their highly ordered closed packed hexagonal structure[9], and the flexibility to modify it by controlling influencing factors during anodization process such as the electrolyte, anodization voltage, process temperature, and duration. Especially, anodization voltage affects strongly on the pore diameter and interpore distance [10].

During anodization process, a barrier oxide at the bottom of each nanopores is formed and it hinders current flowing through template, thus it prevents homogenous filling of catalytic metal nanoparticles which is required in order to synthesize nanostructures inside of pores. Recently, we have introduced barrier layer thinning process by voltage decrease method[11] and this controllable method allows ones to fill uniformly metal nanoparticles inside of pores.

Here, we present a PAA template-based direct synthesis of SiNW arrays using gold nanoparticles as a catalyst. We show how we can adjust precisely the SiNWs diameter by controlling the volume of the electrodeposited gold nanoparticles. We also demonstrate that the size of the SiNWs is strongly dependent on pore size and on the gold nanoparticles volume.

EXPERIMENT

Silicon nanowires were grown inside porous anodic alumina template. Prior to practical SiNWs growth catalyst filling process has been done in PAA templates fabricated in 0.3M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) at room temperature. Depending on desired pore diameter and interpore distance, anodization voltage was varied. After anodization process, barrier layer thinning process so-called exponential voltage decrease was carried out subsequently in order to thin barrier oxide layer at the bottom of nanopores [11]. Then, wet-chemical pore widening process was carried out for a removal of residual barrier oxide layer at the bottom of pores in 0.3M phosphoric acid (H_3PO_4) at 30 °C for 25 min.

For catalyst filling process, pulsed electrodeposition (PED) process was introduced [11, 12]. Here, gold was used as a catalyst for SiNW growth and several influencing parameters on PED process was varied for successful Au filling inside PAA template. Au deposition process was carried out in a mixture solution of 0.93 g/L $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 30 g/L boric acid (H_3BO_3), and applied voltage was mostly – 6.5V. For PED process, very simple pulse shape was introduced, i.e., pulse regime for 5 ms and rest regime for 90 ms in one cycle. Finally, the volume of filled Au was adjusted by varying the number of pulse sweeps.

After successful Au filling process inside nanopores array, SiNW growth process was carried out using modified hot-filament chemical vapor deposition (HF CVD) system as else where described [13, 14]. Silane (SiH_4) as a silicon precursor gas and hydrogen (H_2) as an etching agent of parasitic amorphous silicon were introduced to grow SiNWs, and hot-filament placed at H_2 gas inlet was powered to efficiently decompose H_2 molecules in order to generate atomic hydrogen. Such generated atomic hydrogen can decompose SiH_4 molecules efficiently, and prevent parasitic a-Si deposition resulting in SiNW growth obstruction by pore clogging on the

surface of PAA as well as the wall of nanopores [15]. Growth temperature was varied from 350 °C to 500 °C and total vapor pressure was 5 mbar while the gas composition ratio was kept with 20 sccm SiH₄ and 100 sccm H₂. The duration of SiNW growth was 30 min for all cases.

Filled Au nanoparticles/nanowires and the grown SiNWs inside PAA template were observed by field emission scanning electron spectroscopy (FE SEM, HITACHI S4800) with various applied voltage and emission current and the structural quality of SiNWs was investigated by high resolution confocal Raman microscope (Labram, HR800, HORIBA Jobin Yvon, $\lambda = 633$ nm), in the normal incident backscattering configuration.

RESULTS AND DISCUSSION

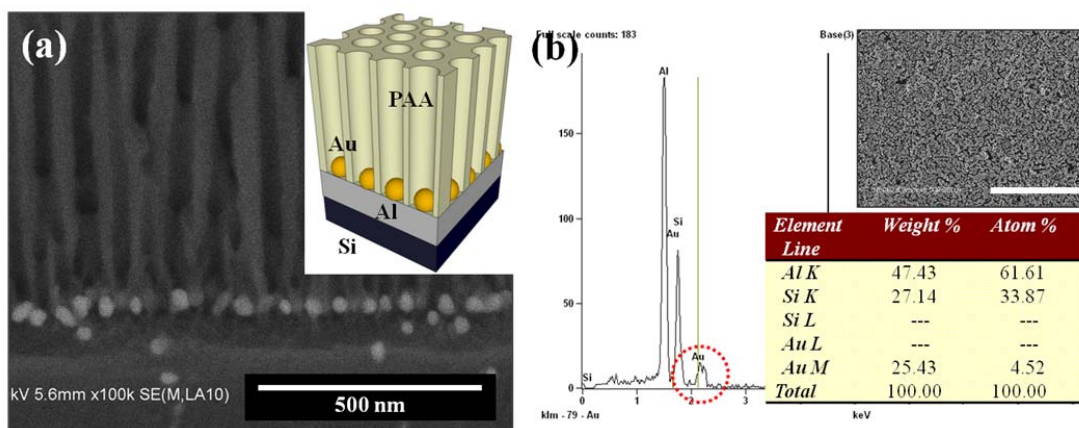


Figure 1. (a) Cross-sectional scanning electron microscopy image of successfully filled gold nanoparticles at the bottom of nanopores in porous anodic alumina template (white particles). Inset shows the schematic image of filled Au nanoparticles inside PAA template. (b) Electron dispersive spectroscopy analysis on filled Au nanoparticles after a removal of PAA template. Inset shows SEM image after a removal of PAA, and table shows weight and atomic percentages of the elements.

Figure 1(a) shows a cross-sectional scanning electron microscopy image after a PAA fabrication and subsequent gold electrodeposition process. It is clearly shown that Au nanoparticles are quite totally filled inside PAA template by barrier layer thinning process and subsequent pulsed electrodeposition process. Moreover, the nature of filled Au nanoparticles inside nanopores was clearly ascertained using electron dispersive spectroscopy analysis as shown in figure 1(b). In order to perform EDS on filled Au nanoparticles more readily, inset shows that PAA was removed using 0.3M H₃PO₄ at 30 °C. However, during the selective removal of PAA template, some aluminum might be etched away by the 0.3M H₃PO₄ resulting in a subsequent removal of Au nanoparticles. Therefore, black spots in inset of figure 1(b) were observed as well. It is evidenced that with such approach, direct filling of Au nanoparticles inside PAA template while aluminum substrate is preserved. Such method is very advantageous that direct fabrication and electrodeposition is possible resulting in direct nanomaterials synthesis inside PAA template without any complicated fabrication process such as detaching PAA and subsequent conducting layer deposition at rare face of PAA in order to carry out metal deposition by barrier layer thinning process and subsequent modified PED process.

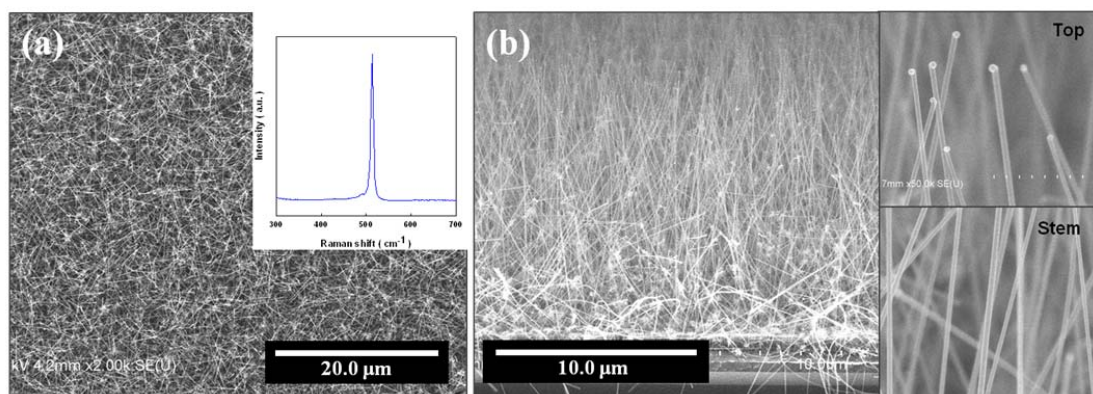


Figure 2. (a) SEM image of grown SiNWs inside PAA template. Inset shows Raman spectra of grown SiNWs. (b) Cross-sectional SEM image of SiNWs inside PAA template.

Figure 2 shows SEM images of grown SiNWs inside PAA template, and it is clearly verified that high density SiNWs were emerged from the bottom of nanopores by direct synthesis method. The structural quality of SiNWs was analyzed using Raman spectroscopy, and it is shown that they are very well crystallized SiNWs as shown in inset of figure 2(a). Moreover, as shown in figure 2(b), emerged SiNWs were mostly in vertical direction with high uniformity in terms of diameter of SiNWs as shown the right images of figure 2(b). We point out that by using such approach, direct synthesis of SiNWs was carried out with very high uniformity and controllability (?). Thus, it is a very powerful tool for direct synthesis of nanomaterials on any substrate without complicated method.

On the other hand, as mentioned previously, direct metal filling method is a very powerful tool for single metal filling (figure 1) as well as multi-layered metal filling as shown in figure 3.

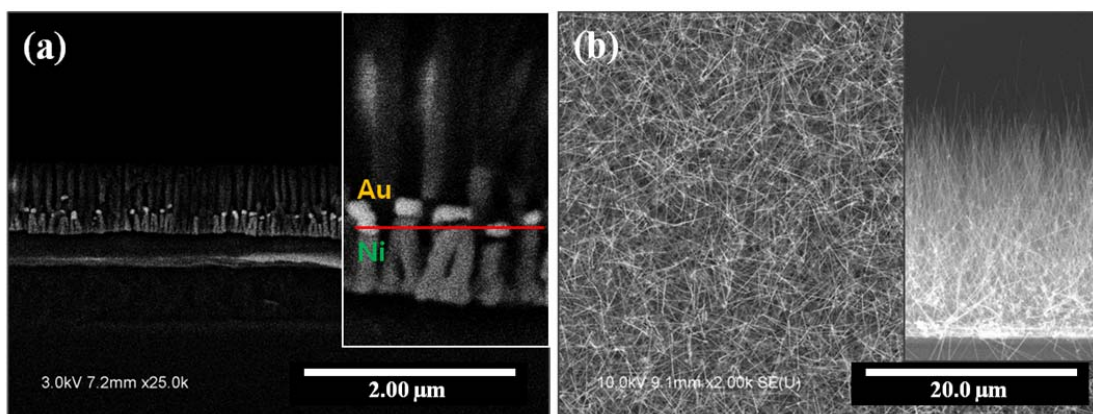


Figure 3. (a) Cross-sectional SEM image of filled Au nanoparticles on pre-filled nickel nanowires inside PAA template. Inset shows magnified SEM image. (b) SEM images of grown SiNWs inside PAA template using multi-layered catalyst. Inset shows cross-sectional SEM image of SiNWs inside PAA template using multi-layered catalyst.

Figure 3(a) shows filled multi-layered metal nanowires of Au and pre-filled Ni. Ni was prefilled inside nanopores prior to Au deposition. As already reported [11, 12], Ni can be well

electrodeposited inside PAA template ($\sim 100\%$), so it was expected that Au filling fraction will be enhanced by Ni prefilling approach yielding multi-layered metal nanowires. Moreover, usually, introducing barrier layer thinning process results in branched structure at the bottom of nanopores [11, 16]. Even though, very well filled small gold nanoparticles could be successfully located inside nanopores as shown in figure 1, one can notice that some of such nanoparticles are placed inside each of the branched structure at the bottom of nanopores. As all of filled gold nanoparticles can catalyze the growth silicon nanowires, silicon nanowires may grow competitively in every single pore. Silicon nanowires are observed to emerge from most of nanopores, but competitively growth can obstruct emerging silicon nanowire outside of nanopores. If gold nanoparticles are larger so that the branched nanopores are fully filled, such bigger gold nanoparticles/nanowires were catalyze the growth of bigger silicon nanowires which leads to non-uniform growth. To this respect, multi-metal filling in which underlying metal is filled to unbranched stem(?) of nanopores could be more advantageous as shown in figure 3(a). Here, multi-layered metal nanowires are clearly evidenced in the inset of figure 3(a) with grain boundary between Au nanoparticles and Ni nanowires. On top of the metal nanowires filled branched nanopores, single gold nanoparticles could be formed inside each nanopore, that subsequently could be used for catalyzing the growth of single silicon nanowires as shown in figure 3(b). Higher density of emerged silicon nanowires from inside of the bottom of nanopores could thus be obtained. Moreover, nearly 100% filled metal nanoparticles such as nickel also yield nearly 100% filling of gold nanoparticles inside nanopores. Inset of figure 3(b) shows cross-sectional SEM image of grown SiNWs inside PAA template using multi-layered metal nanowires.

Another advantage of multi-metal filling rely on the fact that while silicon nanowires are grown using gold nanoparticles as a catalyst, the underlying Ni nanowires can lead to nickel silicide formation which ensure better contact between Ni and underlying Si substrate. Such nickel silicide layer can reduce contact resistance between substrate (in applications where it is to be used as contact electrode) and silicon nanowires [17, 18]. This is very important for practical device application because, contact resistance between silicon nanowires and metal electrode is always the problem which has to be overcome. Although other metals can be used for multi-layered metallic catalysts deposition inside nanopores, nickel is regarded as a preferred underlying metal particle. As a matter of fact, nickel is the one of the easiest metal to fill inside nanopores by electrodeposition process [11, 12]. As already reported by Bernd et al.[11], $\sim 100\%$ nickel nanoparticles could be filled inside nanopores by PED process after barrier layer thinning process. Furthermore, the volume of filled nickel nanoparticles could be adjusted by modifying electrodeposition parameters such as deposition voltage, pulse shape, etc. Thus, nickel nanowires could be readily filled until non-branched stem of nanopores. Another very important advantage of introducing nickel as an underlying metal nanoparticles is that nickel silicide is regarded as one of the most effective materials to make ohmic contact between silicon nanowires and metal electrode to reduce contact resistance [17, 18].

CONCLUSIONS

Very high density of uniformly grown silicon nanowires (SiNWs) with very narrow diameter distribution were successfully organized using directly filled gold (Au) nanoparticles inside porous anodic alumina (PAA) template by pulsed electrodeposition (PED) process

following barrier layer thinning process. Due to direct filling of Au nanoparticles, the volume of Au could be adjusted by controlling electrodeposition parameters directly, and moreover, multi-layered metal PAA pre-filling can enhance the density of Au nanoparticles, and ensure very low contact resistance between SiNWs and metal electrode at the bottom. Thanks to precise control of the size of SiNWs by modifying the size of pores and of the catalytic nanoparticles, such template based synthesis method has great interest for many applications such as field-effect transistors which have 3-D structures, various types of sensors, solar cells, anodes for Li-ion batteries, and so on.

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